



US009194798B2

(12) **United States Patent**
Baba et al.

(10) **Patent No.:** **US 9,194,798 B2**
(45) **Date of Patent:** **Nov. 24, 2015**

(54) **IMAGING BASED REFRACTOMETER FOR
HYPERSPECTRAL REFRACTIVE INDEX
DETECTION**

(71) Applicant: **UT-Battelle, LLC**, Oak Ridge, TN (US)

(72) Inventors: **Justin S. Baba**, Knoxville, TN (US);
Philip R. Boudreaux, Knoxville, TN
(US)

(73) Assignee: **UT-Battelle, LLC**, Oak Ridge, TN (US)

(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 110 days.

(21) Appl. No.: **13/768,802**

(22) Filed: **Feb. 15, 2013**

(65) **Prior Publication Data**

US 2013/0242115 A1 Sep. 19, 2013

Related U.S. Application Data

(60) Provisional application No. 61/610,094, filed on Mar.
13, 2012.

(51) **Int. Cl.**
G01N 21/41 (2006.01)
G01N 21/43 (2006.01)

(52) **U.S. Cl.**
CPC **G01N 21/4133** (2013.01); **G01N 21/43**
(2013.01)

(58) **Field of Classification Search**
CPC G01N 21/553; G01N 2021/212; G01N
2021/215; G01N 21/43; G01N 21/4133;
G01B 11/0625
USPC 356/432–440, 445–448, 630–632,
356/128–137
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,449,051	A	6/1969	Levitt	
4,011,015	A	3/1977	Baba	
4,692,024	A *	9/1987	Bloss	356/135
5,822,073	A *	10/1998	Yee et al.	356/445
6,493,097	B1 *	12/2002	Ivarsson	356/630
7,187,444	B2 *	3/2007	Naya et al.	356/445
7,233,391	B2 *	6/2007	Schermer et al.	356/246
7,619,725	B1	11/2009	Seaver	
7,755,763	B2	7/2010	Anders et al.	
7,879,619	B2 *	2/2011	Jing et al.	436/171
2002/0126290	A1	9/2002	Naya	
2003/0169417	A1 *	9/2003	Atkinson et al.	356/135
2004/0145731	A1	7/2004	Nakajima et al.	

(Continued)

OTHER PUBLICATIONS

U.S. Appl. No. 14/103,746, filed Dec. 11, 2013, Baba.

(Continued)

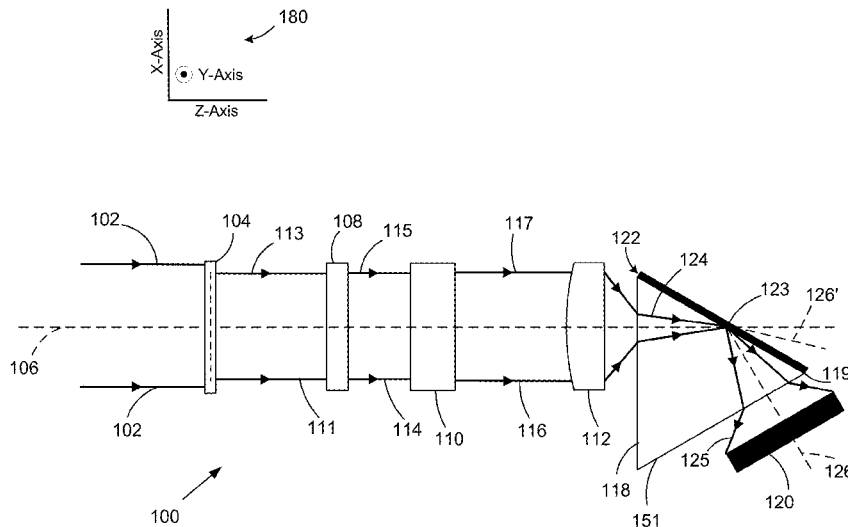
Primary Examiner — Hoa Pham

(74) *Attorney, Agent, or Firm* — Klarquist Sparkman, LLP

(57) **ABSTRACT**

Refractometers for simultaneously measuring refractive index of a sample over a range of wavelengths of light include dispersive and focusing optical systems. An optical beam including the range of wavelengths is spectrally spread along a first axis and focused along a second axis so as to be incident to an interface between the sample and a prism at a range of angles of incidence including a critical angle for at least one wavelength. An imaging detector is situated to receive the spectrally spread and focused light from the interface and form an image corresponding to angle of incidence as a function of wavelength. One or more critical angles are identified and corresponding refractive indices are determined.

28 Claims, 8 Drawing Sheets



(56)

References Cited

U.S. PATENT DOCUMENTS

2011/0194109 A1* 8/2011 Kahre 356/326
2013/0293875 A1 11/2013 Wagner

OTHER PUBLICATIONS

Guo et al., "A Two-Reflection Divergent Differentiating Critical Angle Refractometer," Rev. Sci. Instrum. 82, 053108-1 to -8 (2011).
Guo et al., "A Local Curve-Fitting Method for the Complex Refractive Index Measurement of Turbid Media," Meas. Sci. Technol. 23, 047001 (4pp) (2012).
Baba et al., "Full-Field Imaging-Based Instantaneous Hyperspectral Absolute Refractive Index Measurement," Opt. Lett. 37(9), 1520-1522 (2012).

Boudreaux, Spectroscopy Using Short-Path Surface Plasmon Dispersion, Master of Science Thesis, University of Tennessee, Knoxville (2004).

Castrejón-Pita et al., "Critical Angle Laser Refractometer," Rev. Sci. Instrum. 77, 035101-1 to -4 (2006).

Ferrell et al., "Plasmons and Surfaces," American Scientist 73(4), 344-353 (1985).

Kim et al., "Absolute Refractive Index Measurement Method Over a Broad Wavelength Region Based on White-Light Interferometry," Appl. Opt. 49(5), 910-914 (2010).

Pixton et al., "Automated Measurement of the Refractive Index of Fluids," Appl. Opt. 47(10), 1504-1509 (2008).

* cited by examiner

FIG. 1A

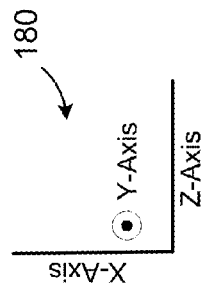
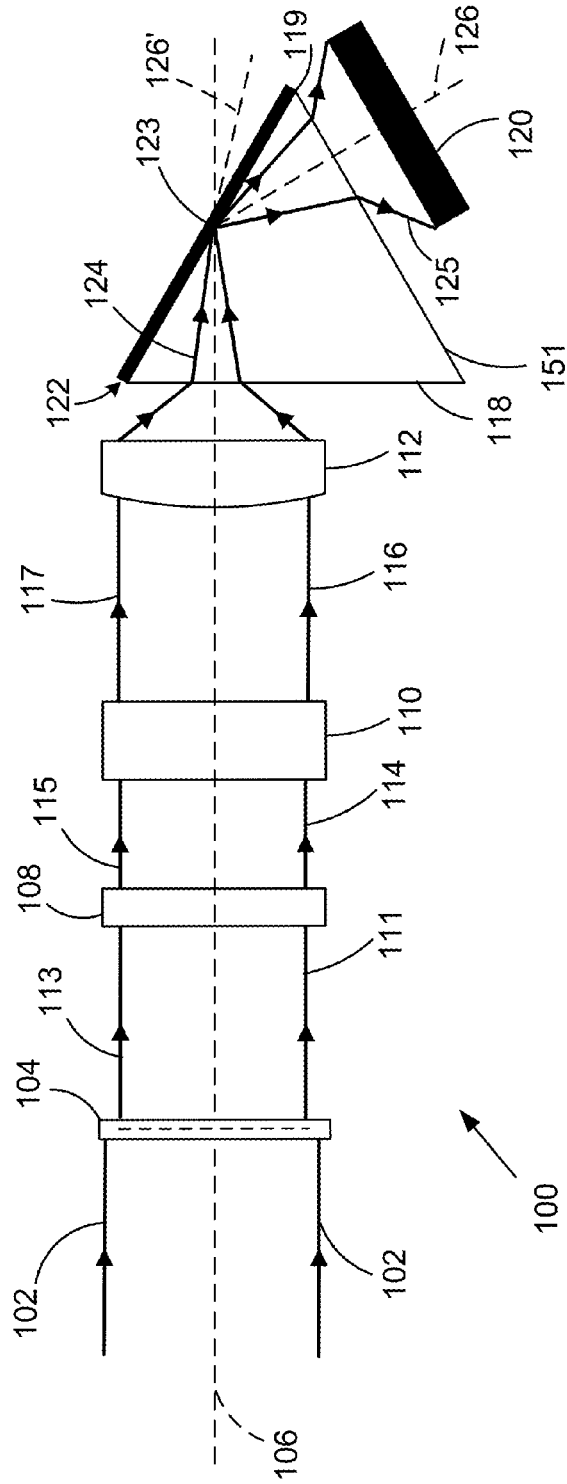
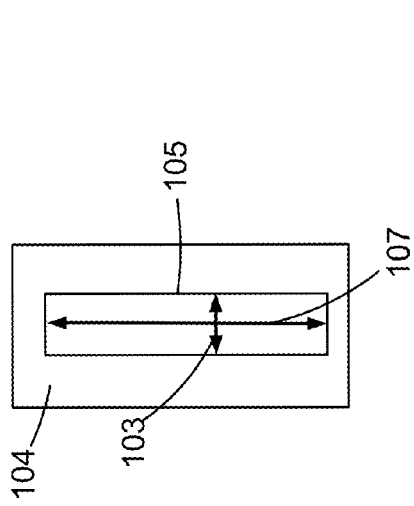


FIG. 1B



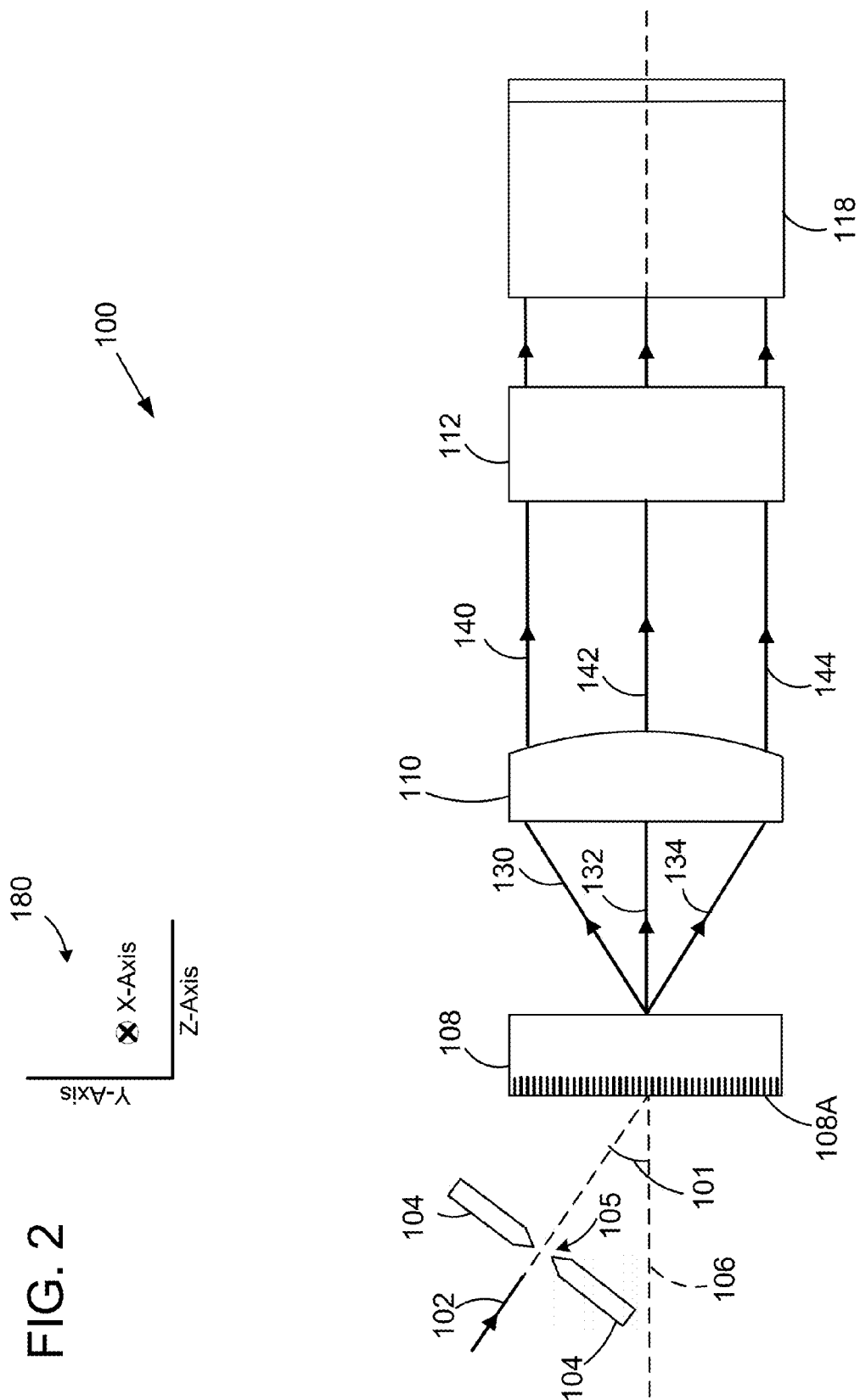
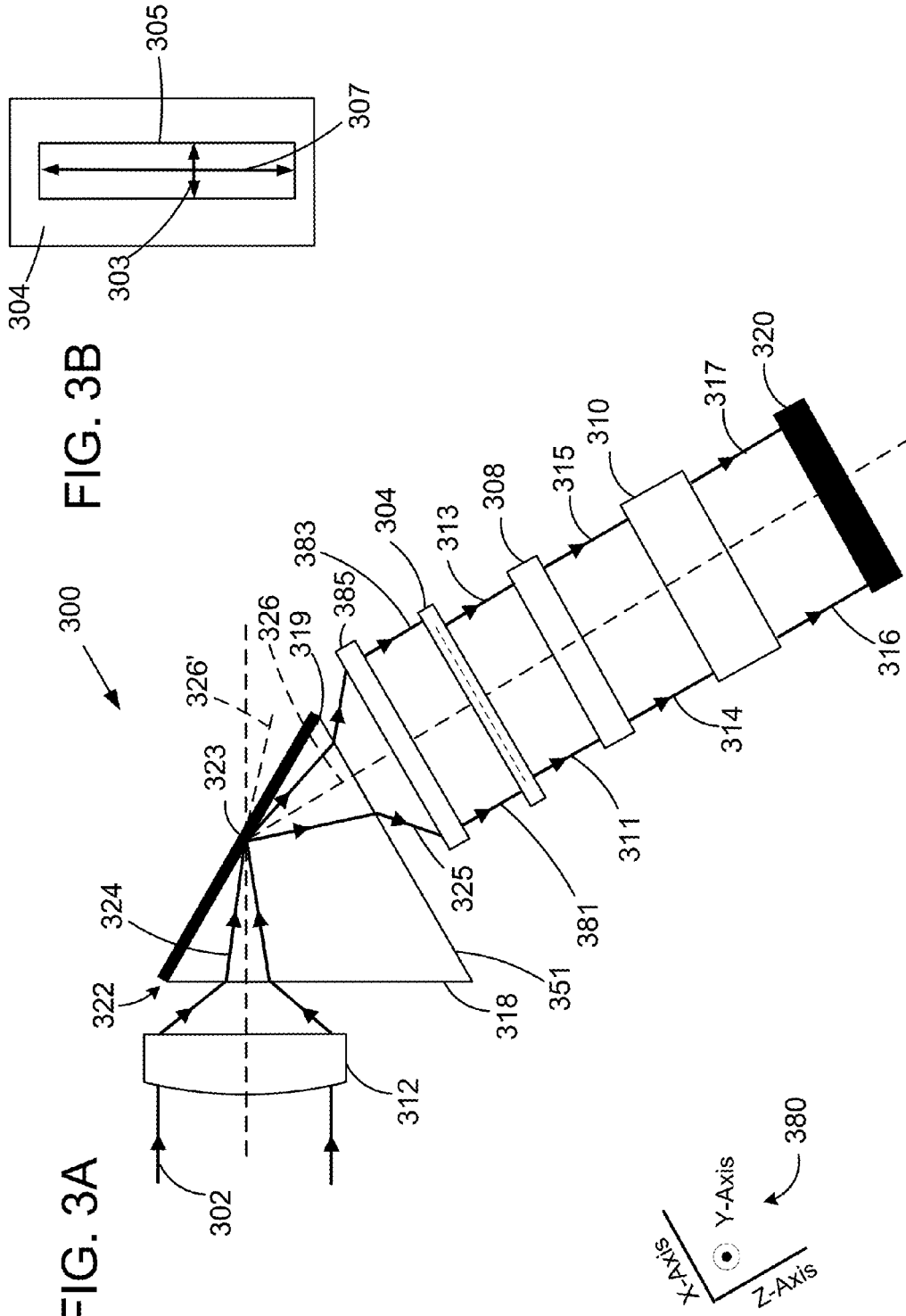


FIG. 3A

FIG. 3B



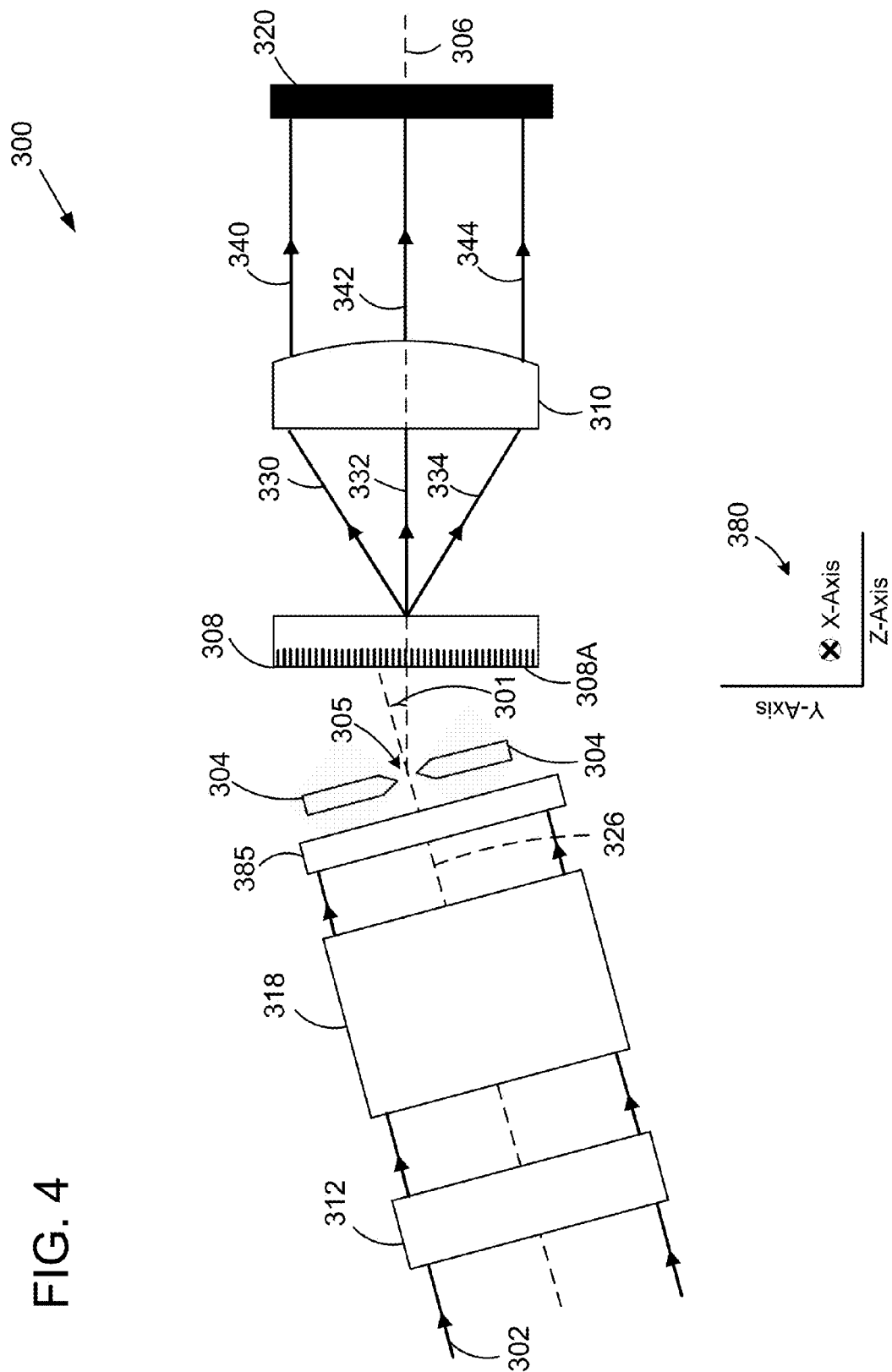


FIG. 5

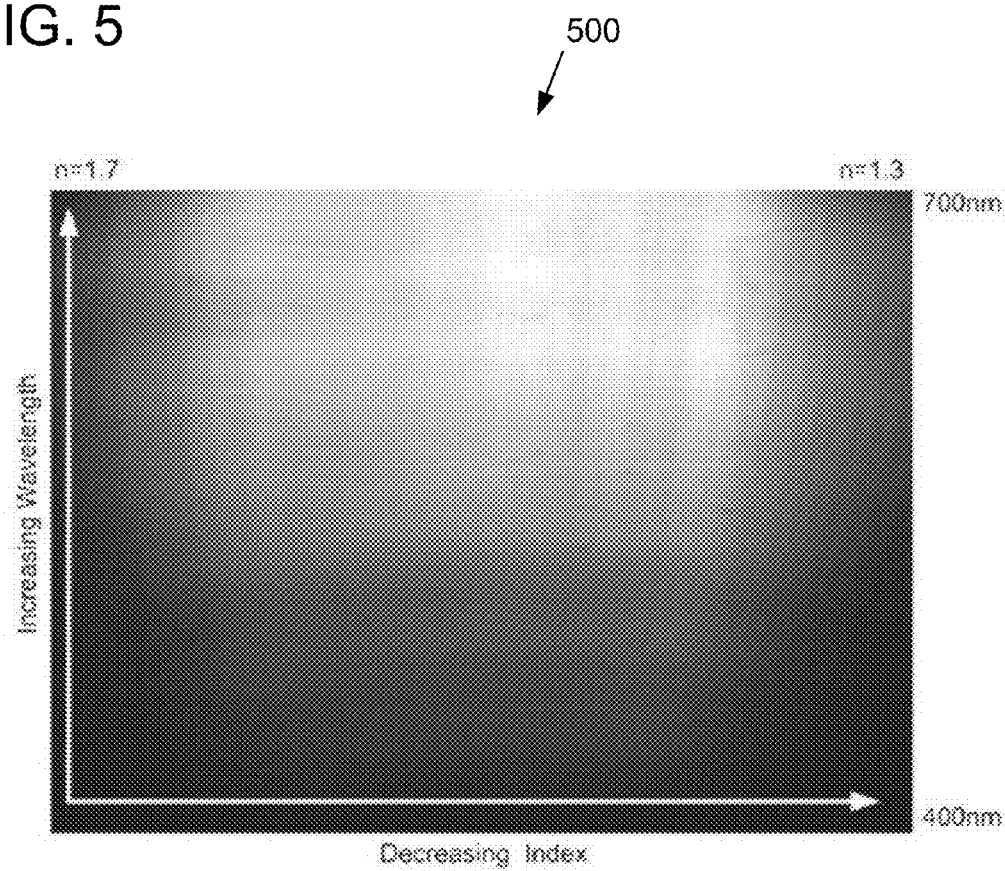


FIG. 6

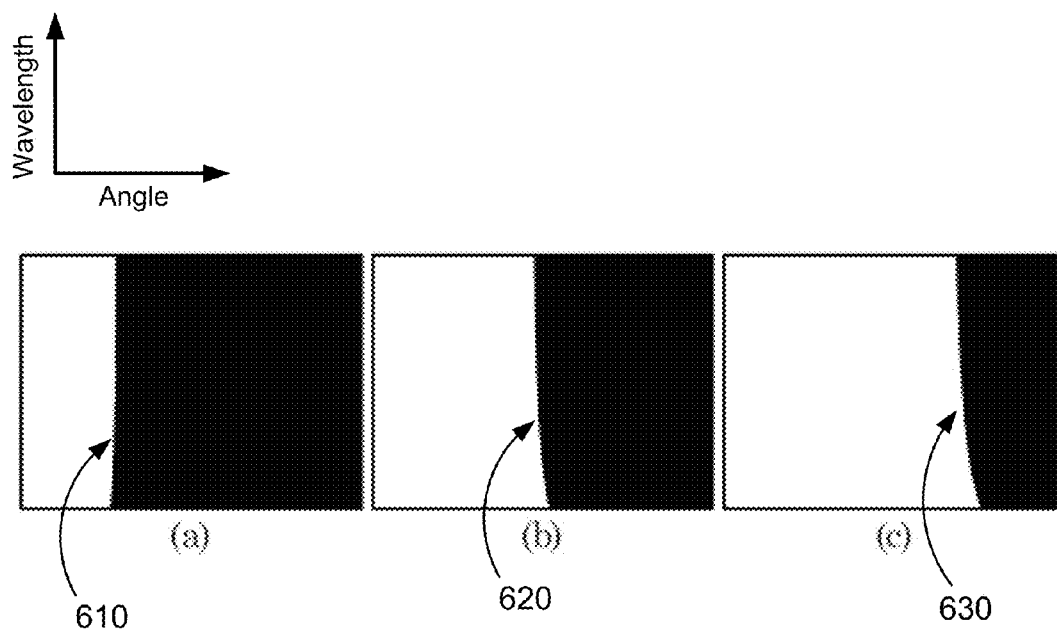


FIG. 7

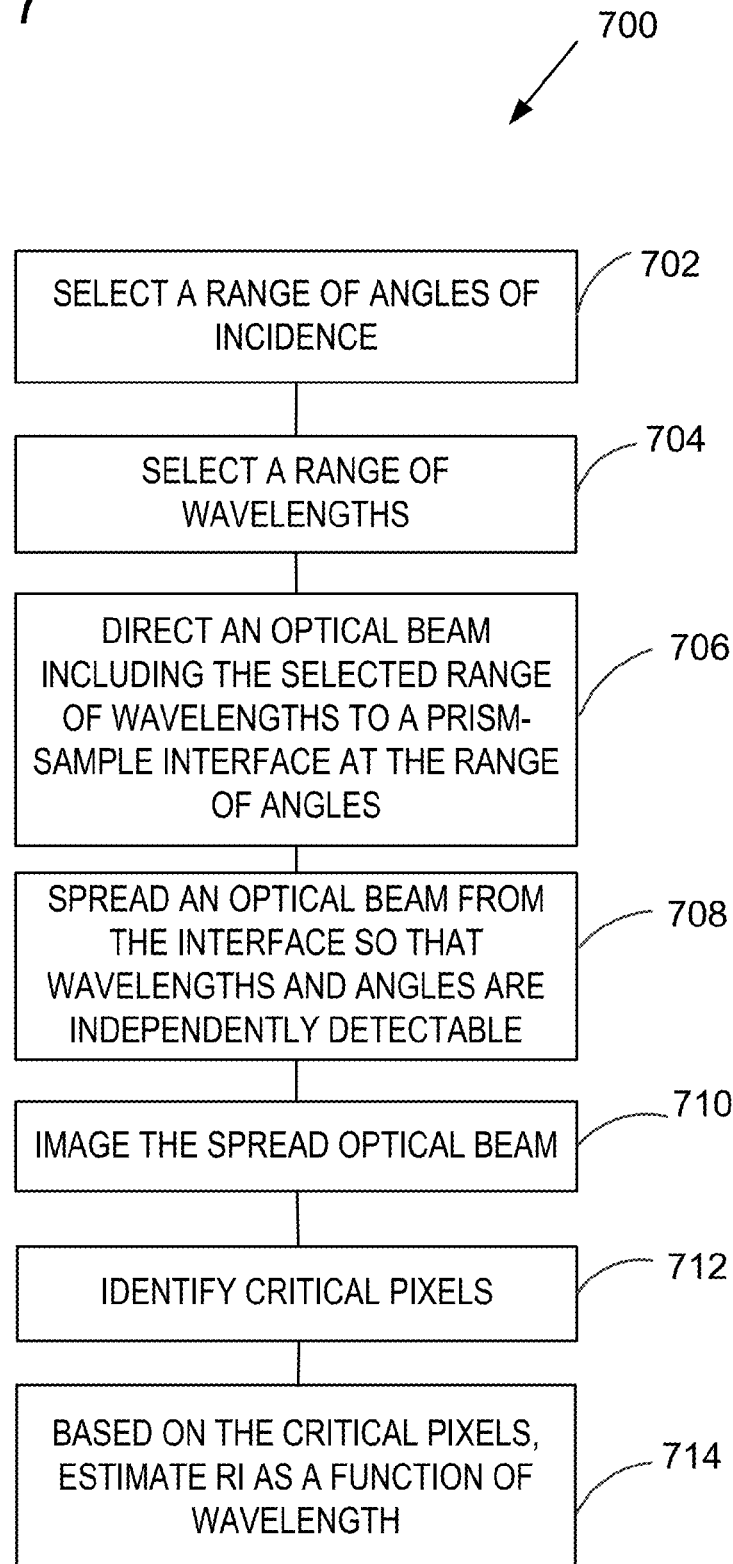
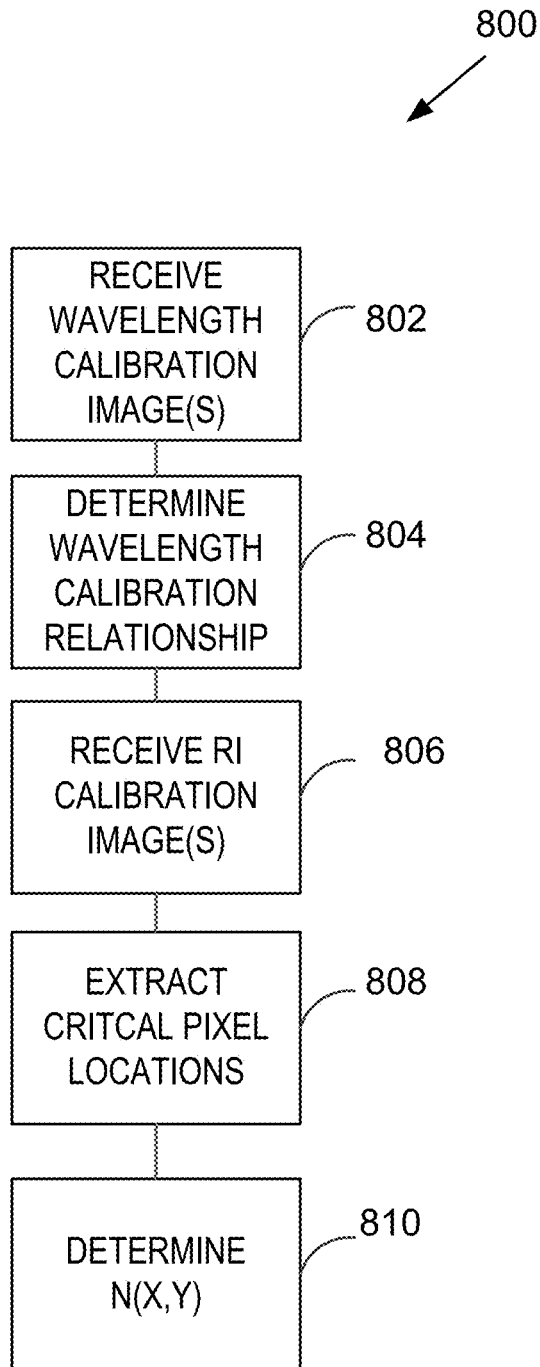


FIG. 8



1

IMAGING BASED REFRACTOMETER FOR HYPERSPECTRAL REFRACTIVE INDEX DETECTION

CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application No. 61/610,094, which is incorporated herein by reference.

ACKNOWLEDGMENT OF GOVERNMENT SUPPORT

This invention was made with government support under Contract No. DE-AC05-00OR22725 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

FIELD

This disclosure pertains to methods and apparatus for measuring refractive index.

BACKGROUND

The refractive index (RI) of a material—that is, the ratio of the speed of light in a vacuum to the speed of light in the material—can be an important property for use in species identification and material characterization. For example, in industries such as food production and pharmaceuticals, RI can be used as a measure of product quality or to characterize reactions and other dynamic processes. More specifically, precise species identification can be achieved using multi-wavelength RI measurement, and the ability to perform real-time or continuous multi-wavelength RI measurements can be useful for monitoring the properties of analytes and other chemical constituents.

Conventional refractometers and techniques for measuring RI have various drawbacks and limitations. For example, conventional refractometers use single wavelength sources or filtered light and are capable of measuring RI only for discrete wavelengths. Multi-wavelength measurement requires moving parts (e.g., rotation of the sample and/or prism(s)) or serial measurements. Consequently, such refractometers have limited ability to observe RI in real-time and to produce continuous dispersion profiles. Thus, new techniques for RI measurements are still needed.

SUMMARY

This Summary is provided to introduce a selection of concepts in a simplified form that are further described below in the Detailed Description. This Summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter.

Refractometers comprise a focusing optical system configured to direct an optical beam that includes a range of wavelengths to be incident on an interface between the sample and a prism at a range of angles of incidence including a critical angle, and a dispersive optical system configured to spectrally spread the optical beam so that the range of wavelengths and the critical angle are independently detectable. In some examples, the dispersive optical system comprises a diffraction grating configured to spectrally spread the optical beam by imposing a wavelength dependent angular dispersion

2

along a first axis and a cylindrical lens configured to collimate the spectrally spread optical beam along the first axis to produce a collimated spectrally spread optical beam. In representative embodiments, refractometers comprise a detector configured to receive the spectrally spread optical beam and to generate one or more two-dimensional images having pixel coordinates associated with the range of wavelengths and the range of angles of incidence. The prism can be an equilateral sapphire or SF10 optical glass prism. However, the prism materials are not limited to SF10 or sapphire. In some implementations, refractometers comprise a light source configured to produce the optical beam and so that the optical beam is substantially collimated and a slit is oriented so that a longer dimension is substantially perpendicular to the first axis and configured to reduce spectral overlap in the spectrally spread optical beam.

In some examples, the focusing optical system comprises a cylindrical lens configured to focus the collimated spectrally spread optical beam along a second axis substantially perpendicular to the first axis so as to establish the range of angles of incidence. In other examples, the focusing optical system comprises a second cylindrical lens situated upstream from the dispersive optical system and configured to focus the optical beam along a second axis substantially perpendicular to the first axis so as to establish the range of angles of incidence. In further examples, refractometers comprise a collimating optical system configured to receive the optical beam from the interface between the sample and the prism and to direct a substantially collimated optical beam to the diffraction grating.

Refractometers comprise a dispersive optical system configured to receive a collimated optical beam and to spectrally disperse a range of wavelengths of the optical beam along a first axis. A first cylindrical lens is configured to collimate the spectrally dispersed optical beam along the first axis, and a second cylindrical lens is configured to converge the collimated spectrally dispersed light along a second axis that is not parallel to the first axis. A prism having a surface configured to contact a sample is situated to receive the converged optical beam at an interface between the surface and the sample. A detection system is situated and configured to detect critical angles of the sample for at least two wavelengths of the range of wavelengths. The second cylindrical lens and the prism can be configured to produce critical angle total internal reflection at the interface over at least a portion of the range of wavelengths. The prism can be an equilateral prism. In some examples, the dispersive optical system comprises a diffraction grating having grooves oriented parallel to the second axis.

In some implementations, refractometers comprise a slit with a longer dimension oriented parallel to the second axis and configured to reduce spectral overlap of the spectrally dispersed optical beam produced by the dispersive optical system, wherein the slit is situated at an angle relative to the diffraction grating so that a first order of diffracted light is collected by the first cylindrical lens. In representative examples, refractometers include a sample holder configured to maintain the contact between the surface of the prism and the sample and including a channel to enable flow-through of the sample. The sample can be a gas, a liquid or a liquid-gel. In some examples, refractometers comprise a light source configured to produce the collimated optical beam.

Methods of measuring refractive index of a sample at a plurality of wavelengths comprise directing an optical beam that includes optical radiation at the plurality of wavelengths so as to be incident on an interface between the sample and a prism at a plurality of angles of incidence and spectrally

spreading the optical beam to determine if the plurality of angles of incidence includes a critical angle for one or more of the plurality of wavelengths. In some examples, the methods further comprise identifying a critical angle for at least one of the plurality of wavelengths and/or determining a refractive index of the sample at at least one of the plurality of wavelengths. In representative embodiments, the methods comprise generating at least one two-dimensional image having a first axis corresponding to at least a portion of the plurality of wavelengths and a second axis corresponding to at least a portion of the plurality of angles of incidence. In further examples, the methods comprise determining refractive index of the sample as a function of wavelength from the at least one two-dimensional image.

In some implementations, the spectrally spreading of the optical beam comprises imposing a wavelength dependent angular dispersion on the optical beam along a first axis and collimating the angularly dispersed optical beam to produce a collimated spectrally dispersed optical beam. In further implementations, the directing of the optical beam comprises focusing the collimated spectrally dispersed optical beam along a second axis that is not parallel to the first axis so as to generate the range of angles of incidence. In some examples, the first axis is perpendicular to the second axis.

Methods of refractive index measurement comprise, identifying critical pixel locations from one or more images, and estimating refractive index for the test sample at at least two wavelengths of the plurality of wavelengths using a refractive-index-calibration relationship and the identified critical pixel locations. In some examples, the methods comprise deriving a wavelength-calibration relationship expressing wavelength as a function of one or more pixel coordinates using a set of wavelength calibration images collected with one or more light sources having known emission spectra, wherein the estimating of the refractive index is based on the wavelength-calibration relationship. In other examples, the methods comprise deriving the refractive-index-calibration relationship using a set of refractive index calibration images collected using one or more calibration samples having known refractive index dispersion profiles, wherein the refractive-index-calibration relationship expresses measured refractive index as a function of critical pixel location.

The foregoing and other features and advantages will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a side view of a representative critical angle refractometer.

FIG. 1B is a front view an aperture plate defining a slit.

FIG. 2 is a top view of the refractometer of FIG. 1A.

FIG. 3A is a side view of a representative critical angle refractometer in which spectral dispersion is produced after light interacts with a prism-sample interface.

FIG. 3B is a front view of an aperture plate defining a slit.

FIG. 4 is a top view of the refractometer of FIG. 3A.

FIG. 5 is a representative image produced by a refractometer with no sample.

FIG. 6A-6C illustrates representative images of samples with three different refractive index profiles.

FIG. 7 is a representative method of multi-wavelength measurement of refractive index of a sample.

FIG. 8 is a representative method of refractometer calibration.

DETAILED DESCRIPTION

The following disclosure is presented in the context of representative embodiments that are not to be construed as being limiting in any way. This disclosure is directed toward all novel and non-obvious features and aspects of the various disclosed embodiments, alone and in various combinations and sub-combinations with one another. The disclosed methods, apparatus, and systems are not limited to any specific aspect or feature or combination thereof, nor do the disclosed embodiments require that any one or more specific advantages be present or problems be solved.

Although the operations of the disclosed methods are described in a particular, sequential order for convenient presentation, it should be understood that this manner of description encompasses rearrangement of the operations, unless a particular ordering is required by specific language set forth below. For example, operations described sequentially may in some cases be rearranged or performed concurrently. Moreover, for the sake of simplicity, the attached figures may not show the various ways in which the disclosed systems, methods, and apparatus can be used in conjunction with other things and methods.

This disclosure sometimes uses terms like “produce,” “generate,” “select,” “receive,” “exhibit,” and “provide” to describe the disclosed methods. These terms are high-level abstractions of the actual operations that are performed. The actual operations that correspond to these terms may vary depending on the particular implementation and are readily discernible by one of ordinary skill in the art.

The singular forms “a,” “an,” and “the” include the plural forms unless the context clearly dictates otherwise. The term “includes” means “comprises.” Unless the context dictates otherwise, the term “coupled” means mechanically, electrically, or electromagnetically connected or linked and includes both direct connections or direct links and indirect connections or indirect links through one or more intermediate elements not affecting the intended operation of the described system.

Certain terms may be used such as “top,” “side,” “front,” “back,” and the like. These terms are used, where applicable, to provide some clarity of description when dealing with relative relationships. But, these terms are not intended to imply absolute relationships, positions, and/or orientations.

The term “or” refers to a single element of stated alternative elements or a combination of two or more elements, unless the context clearly indicates otherwise.

Unless explained otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this disclosure belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, suitable methods and materials are described below. The materials, methods, and examples are illustrative only and not intended to be limiting. Other features of the disclosure are apparent from the following detailed description and the claims.

Unless otherwise indicated, all numbers expressing quantities of components, percentages, temperatures, times, and so forth, as used in the specification or claims are to be understood as being modified by the term “about” or “approximately.” Accordingly, unless otherwise indicated, implicitly or explicitly, the numerical parameters set forth are approximations that may depend on the desired properties

sought and/or limits of detection under standard test conditions/methods. When directly and explicitly distinguishing embodiments from discussed prior art, the embodiment numbers are not approximates unless the word “about” is recited.

Refractometers described herein use critical angle total internal reflection to determine the refractive index (RI) of a sample. The critical angle is the angle at which light incident on an interface between two media having different RIs (e.g., n_1 and n_2) transitions from partial transmission to complete reflection (total internal reflection (TIR)). TIR occurs at the critical angle and at angles of incidence greater than the critical angle. According to Snell’s law, the critical angle θ_c is defined as follows:

$$\theta_c = \sin^{-1}(n_2/n_1), \text{ where } n_1 > n_2.$$

Because the RI of a material is typically a function of wavelength, critical angle also varies as a function of wavelength.

In examples of the disclosed critical angle refractometers, a sample is placed in contact with a surface of a prism with a known RI. The critical angle is measured by directing light to the prism surface in contact with the sample and detecting light reflected at the prism-sample interface. The reflected light can be detected using an imaging detector such as a charge-coupled device (CCD) or other imaging device suitable for detecting the wavelengths associated with the light. The imaging detector is configured to produce an image that can be displayed or stored. The produced images include a transition region in which pixel intensities transition from dark to light (e.g., detected light intensity transitions from relatively low intensity to relatively high intensity). This indicates the transition from partial transmission to TIR that occurs at the critical angle and at angles of incidence greater than the critical angle. Image pixel(s) corresponding to this transition region can be referred to as critical pixel(s) P_c .

The critical angle can be determined based on critical pixel location in the image. The index of refraction is then calculated from the critical angle using Snell’s law as discussed above. For a critical angle refractometer, n_1 is the index of refraction of the prism, and n_2 is the index of refraction of the sample. Because the index of refraction of the prism is known, the RI of the sample is determined by measuring the critical angle θ_c .

FIGS. 1-4 illustrate representative critical angle refractometers that enable multi-wavelength measurement of RI of a sample. That is, RI can be measured for a range of wavelengths either sequentially or simultaneously. As used herein, a range of wavelengths includes a plurality of wavelengths and can be a continuous or non-continuous plurality of wavelengths. The refractometers described herein can provide for hyperspectral measurement of RI.

FIG. 1A is a side view of a representative refractometer 100, and FIG. 2 is a top view of the refractometer of FIG. 1A. In the following discussion, references to an xyz-coordinate system 180 are made to facilitate convenient description of the refractometer 100. As shown in FIG. 1A, a y-axis extends outwardly from the plane of FIG. 1A. As shown in FIG. 2, the x-axis extends into the plane of FIG. 2. The coordinate system 180 is provided only to simplify the description, and the refractometer 100 is not limited to particular arrangement in any coordinate system.

Referring to FIGS. 1A and 2, a collimated optical beam 102 is directed to an aperture plate 104 that defines a slit 105, which produces an optical beam 111, 113. FIG. 1B is a front enlarged view of the aperture plate 104 and illustrates the dimensions of the slit 105. As shown in FIG. 1B, the slit 105 has a shorter dimension 103 (width W) and a longer dimension 107 (length L) perpendicular to the shorter dimension in

a plane defined by the aperture plate 104. The aperture plate 104 is situated within the refractometer 100 so that the longer dimension 107 is parallel to the x-axis.

The optical beam 102 is substantially collimated at least along the width W of the slit 105 (i.e., in the yz-plane). The optical beam 102 can be multi-wavelength light (e.g., generated by a broadband white light source, an infrared source, etc.), or the optical beam 102 can be monochromatic (e.g., generated by a discrete wavelength source or using filters). The light source (not shown) for the optical beam 102 produces optical radiation in a range or spectrum of wavelengths over which an RI measurement is to be made. For example, to measure the RI of a sample for wavelengths between 400 nm and 700 nm, the source for the optical beam 102 includes at least wavelengths ranging from 400 nm to 700 nm. In some examples, multiple sources are used.

In general, dimensions of the slit 105 are selected in association with the angular spread of the optical beam 102 and to minimize or reduce spectral overlaps. Typically, the optical beam 102 is substantially collimated and the slit width W is selected so as to reduce or eliminate spectral overlap in the diffracted optical beam produced by the diffraction grating 108. For example, the slit 105 can reduce the angular spread of a transmitted optical beam in the yz-plane, as shown by ray lines 111, 113, to improve collimation of the optical beam 102. Wide slits are associated with greater spectral overlap and reduced spectral resolution, but do permit higher power in the diffracted optical beam.

Because the slit 105 can reduce the intensity of the optical beam entering the refractometer thereby reducing signal-to-noise ratio, it is generally preferred to select a relatively large slit width W. For example, the slit width W can be 10, 100, 200, 500 or 1000 times a central wavelength or other wavelength associated with the optical beam 102. The slit length L is typically much larger than the width W and is selected based on the preferred size of the transmitted optical beam in the xz-plane. For example, the length L can be approximately the same size or greater than the aperture of cylindrical lenses 110 or 112 in the xz-plane. In some implementations, the slit 105 may not be needed. For example, spectral resolution of the refractometer 100 may be sufficient without use of the slit 105.

Referring to FIG. 1, the transmitted optical beam is received along the ray lines 111, 113 by a diffraction grating 108. The grating 108 is situated so as to produce a spectrally dispersed beam 114, 115. Referring to FIG. 2, a groove layer 108A of the grating 108 includes grooves oriented parallel to the x-axis and parallel to the longer dimension 107 of the slit 105. The grating 108 diffracts the optical beam transmitted by the slit 105 within the yz-plane, as illustrated by ray lines 130, 132, 134. The transmitted optical beam is spectrally spread by the grating 108 to form a spectrally dispersed optical beam that propagates as shown by ray lines 114, 115 and with wavelength varying in the yz-plane as a function of distance from (or angle of propagation relative to) an optical axis 106.

Although the grating 108 is illustrated as a transmissive grating, the refractometer 100 can be modified to instead include a reflective grating. In general, spectral resolution of the refractometer depends at least in part on the dispersive effect of the grating 108. Thus, the grating 108 is preferably configured to produce a large dispersion. That is, the grating 108 can be configured to produce a large angular or spatial dispersion or spreading of incident wavelengths (i.e., spectral dispersion). Since such angular spread or separation of wavelengths increases as groove or slit separation decreases, the grating can have a groove or slit spacing that is on the order of the wavelength being measured. For example, groove spacing

can be less than about 1.5, 2, 3, 4 or 5 times a central wavelength or other wavelength associated with the optical beam 102. The grating 108 can be an enhanced resolution transmission grating, a blazed grating, a holographic grating, or other spectrally dispersive element. Additionally, any other dispersive optical components configured to separate spectral components of an optical beam such as prisms can be used.

As shown in FIG. 2, the optical beam 102 can be oriented at an angle 101 relative to the optical axis 106. The angle 101 can be selected so that a selected range of wavelengths at which critical angle is to be measured is approximately centered on the optical axis 106. For example, ray lines 130, 134 represent directions of propagation of maximum and minimum wavelengths within the selected wavelength range. Ray line 132 represents a direction of propagation of a central wavelength within the selected wavelength range. Ray lines 130, 132, 134 are typically associated with a first diffraction order produced by the grating 108, but other diffraction orders can be used.

The spectrally dispersed beam 114, 115 produced by the diffraction grating 108 is received by a first cylindrical lens 110 to produce a collimated, spectrally dispersed beam as indicated by ray lines 116, 117, 140, 144. The cylindrical lens 110 is positioned and oriented so as to collimate the spectrally dispersed beam in the direction of the diffraction produced by the grating 108. That is, the cylindrical lens 110 collimates the spectrally spread beam in the yz-plane, and the optical beam produced by the cylindrical lens 110 is also spectrally separated. For example, as shown in FIG. 2, the cylindrical lens 110 redirects the light propagating according to the ray line 130 along a ray line 140, the light propagating according to the ray line 132 along a ray line 142, and the light propagating according to the ray line 134 along a ray line 144. As shown, the ray lines 140, 142, 144 are substantially parallel to but spatially separated from each other at the output of the cylindrical lens 110. As shown in FIG. 1A by the ray lines 116, 117, the optical beam produced by the cylindrical lens 110 is unchanged in the xz-plane and remains collimated in the xz-plane. Typically, the grating 108 and the cylindrical lens 110 are separated by a focal length of the cylindrical lens 110 so that the spectrally dispersed beam 114, 115 is collimated in the yz-plane.

An aperture of the cylindrical lens 110 can be selected so as to sufficiently collect diffracted light associated with the selected wavelength range. For example, the size and focal length of the cylindrical lens 110 can be selected so that, based on the divergence angles of the ray lines 130, 134 and the separation of the grating 108 and the cylindrical lens 110, the selected wavelength range is collected by the cylindrical lens 110 and has sufficient spatial separation. For example, it may be desirable to have the spatial separation of the wavelengths correspond to dimensions of a detector 120 so as to fill an active area of the detector 120. In some implementations, spectral dispersion can be increased by increasing the focal length of the cylindrical lens 110 and/or by increasing the spatial separation of the wavelengths independent of the angular spread of the wavelengths introduced by the grating 108.

The cylindrical lens 110 directs the collimated, spectrally dispersed beam 116, 117 to a second cylindrical lens 112, which is configured so as to focus the received light on or near an interface 119 between a prism 118 and a sample 123. The sample 123 is held in contact with the prism 118 using a sample holder 122.

The cylindrical lenses 110 and 112, as well as other lenses and optical components described herein, can be achromatic and/or include anti-reflection coatings. For example, the

cylindrical lens 112 and/or the cylindrical lens 110 can be made from materials with low chromatic aberration for the range of wavelengths being measured. Quartz optics, which can have reduced RI dispersion in the visible wavelengths when compared to other materials such as BK7 or other optical glasses, may be used.

The optical beam produced by the cylindrical lens 112 at the interface 119 is spectrally dispersed along the y-axis and has a range of angles of incidence in the xz-plane. That is, the cylindrical lens 112 produces a focal line at the prism-sample interface 119, and the cylindrical lens 112 is oriented so that the focal line is parallel to the y-axis. Focusing the light at the prism-sample interface 119 ensures that the light is incident on the interface 119 between the prism 118 and the sample 123 at a range of angles. The angles of incidence are measured relative to a line perpendicular to the prism-sample interface. In order to increase the range of angles of incidence, the focal length of the cylindrical lens 112 can be decreased. Preferably, the range of angles of incidence includes the critical angle of the interface 119. For the critical angle and angles greater than the critical angle, light incident on the interface 119 between the prism 118 and the sample 123 is totally internally reflected and directed along an axis 126. For angles less than the critical angle, light is refracted and transmitted along an axis 126' and can be partially reflected along axis 126.

The sample 123 can take various forms (i.e., liquid, gas, liquid-gel, etc.) and can be made to contact the surface of the prism 118 using various techniques. For example, the sample 123 can be a liquid placed directly on the surface of the prism 118. A slide can be placed on the sample 123 to facilitate contact with the prism surface. In other examples, a sample holder 122 is used. In one example, the sample holder 122 includes a glass or plastic substrate (e.g., a polymer such as acetal or other similar material) housing a channel configured to retain the sample 123. The sample holder 122 is then configured to be secured to the prism 118 so that the sample 123, while in the channel, is in contact with the prism 118. The sample holder 122 can be black in color in order to reduce light reflection (e.g., from a sample holder-air interface). The sample holder 122 can be configured to allow flow-through of liquid or gaseous samples. In some examples, the channel is connected to a sample source so that a sample under investigation can be continually flowed through the channel as RI measurements are made.

The light produced by the cylindrical lens 112 is refracted, as shown by ray line 124, upon entering the prism 118. Light reflected off of the prism-sample interface is directed to and received by a detector 120, such as a CCD sensor or other sensor capable of detecting the selected wavelength range. The detector 120 can be a full-field sensor, capable of generating a two-dimensional image from the detected light intensity. Images can be stored or displayed. Images can be collected over a predetermined period of time and/or averaged to reduce signal-to-noise ratio. For example, the images can be time integrated. The RI of the sample can be estimated from the images, as described in more detail below.

The detector 120 is positioned on the axis 126 so as to receive the light reflected from the prism-sample interface 119. The position of the detector 120 along the axis 126 relative to the prism 118 can be determined based on the active area of the detector and the desired angular resolution. In some implementations, the refractometer 100 may be configured so that the position of the detector 120 is adjustable.

In general, the resolution of the refractometer 100 can be increased when the detector 120 has a large active area, e.g., when the detector 120 is a large CCD array. However, the

refractometer may be less efficient when the active area is larger than the dimensions of the collected light 125. The minimum desired active area is based on several factors, such as the RI of the prism 118, the size of the cylindrical lens 110, the cylindrical lens 112 and the prism 118, as well as the focal length of the cylindrical lens 112 and the distance between the detector 120 and the prism 118. For example, if the detector 120 is positioned at a distance from the prism 118 so as to receive light 125 when the light 125 has expanded to approximately the same size as light at the output of cylindrical lens 112, the refractometer 100 may be most efficient if the active area of the detector 120 is approximately the same size as the light at the output of the cylindrical lens 112 (i.e., the light represented by ray lines 140 and 144 in the yz-plane and by ray lines 116 and 117 in the xz-plane). In this manner, the detector 120 is positioned to detect the entire range of angles of incidence at the prism-sample interface, and the active area of the detector 120 is completely filled.

The detector 120 can be positioned closer to the prism (i.e., by decreasing the distance between the detector 120 and the prism 118 along the axis 126). However, the detector 120 will detect a range of angles of incidence with less beam spread at the detector and potentially less angular resolution. The detector can also be positioned further from the prism (i.e., by increasing the distance between the detector 120 and the prism 118 along the axis 126). In this case, the entire range of angles of incidence may not be collected unless the active area of the detector 120 is increased. However, angular resolution is increased. Angular resolution can also be increased by reducing the focal length of the cylindrical lens 112 or otherwise increasing the numerical aperture of the focused line.

Although the detector 120 is illustrated as receiving light reflected at the interface 119 of the prism 118 and the sample 123, the refractometer 100 can be re-configured so that the detector 120 receives transmitted light. For example, the detector 120 can be positioned along the side of the prism 118 with the sample 123 and positioned in the path of refracted, transmitted light along the axis 126'.

Although the prism 118 is illustrated as an equilateral prism, other types of prisms can be used. For example, a right angle prism such as a 30-60-90 prism can be used. However, the location of the detector 120 should be adjusted accordingly based on the shape of the prism and standard ray tracing techniques so that the detector 120 continues to receive the light reflected/transmitted from the prism-sample interface 119. It may be desirable to select a prism shape so as to avoid TIR of the light at the prism-air interface surface 151 that receives light reflected off the prism-sample interface 119. Entrance and exit surfaces at the prism 118 can be coated or uncoated. In some examples, the prism is a glass block or slab or a dielectric substrate that does not have a triangular-shaped geometry.

The refractive index of the prism 118 is selected based on the anticipated refractive index of the sample 123. Specifically, in order for total internal reflection to occur at the interface 119 between the sample 123 and the prism 118, the RI of the prism 118 must be higher than the RI of the sample 123. Because the RI of the prism 118 theoretically defines the maximum RI that can be measured by the refractometer 100, it is generally preferred to select a prism 118 with a high RI. For example, the prism 118 can be made of SF10 optical glass or sapphire when the range of wavelengths being measured is part of the visible spectrum. The prism 118 can be made of silicon or germanium when RI measurements are made using infrared wavelength sources. However, other materials can also be used. In addition, choosing a prism 118 with a high RI

can improve wavelength resolution for long wavelengths where dispersion effects of the prism compromise TIR resolvability.

FIGS. 3-4 illustrate a representative critical angle refractometer 300 in which spectral dispersion is produced after light interacts with a prism-sample interface. FIG. 3A is a side view of the refractometer 300, and FIG. 4 is a top view of the refractometer of FIG. 3A. In the following discussion, references to an xyz-coordinate system 380 are made to facilitate convenient description of the refractometer 300.

Referring to FIGS. 3A and 4, a collimated optical beam 302 is directed to a cylindrical lens 312 configured to focus the collimated optical beam on an interface 319 between a prism 318 and a sample 323. The optical beam 302 is substantially collimated in at least an xz-plane. The sample 323 is held in contact with the prism 318 using a sample holder 322. The optical beam 302 can be multi-wavelength light (e.g., generated by a broadband white light source, an infrared source, etc.), or the light can be monochromatic (e.g., generated by a discrete wavelength source or using filters). The light source (not shown) produces optical radiation that includes a range or spectrum of wavelengths over which the RI measurement is to be made.

The cylindrical lens 312 is situated to produce a focal line at the prism-sample interface 319. The cylindrical lens 312 is oriented so that the focal line is parallel to the y-axis. Focusing the light at the prism-sample interface ensures that the light is incident on the interface 319 between the prism 318 and the sample 323 at a range of angles. In order to increase the range of angles of incidence, the focal length of the cylindrical lens 312 can be decreased. Preferably, the range of angles of incidence includes the critical angle of the interface 319. For the critical angle and angles greater than the critical angle, light incident on the interface 319 between the prism 318 and the sample 323 is totally internally reflected and directed along an axis 326. For angles less than the critical angle, the optical beam is typically partially transmitted and reflected.

The sample 323 can take various forms (i.e., liquid, gas, liquid-gel, etc.) and can be made to contact the surface of the prism 318 using various techniques. For example, the holder 322 can be the same or substantially the same as the sample holder 122 described above with respect to FIGS. 1A and 2.

The refractive index of the prism 318 is selected based on the anticipated refractive index of the sample 323. Specifically, in order for total internal reflection to occur at the interface 319 between the sample 323 and the prism 318, the RI of the prism 318 must be higher than the RI of the sample 323. Because the RI of the prism 318 theoretically defines the maximum RI that can be measured by the refractometer 300, it is generally preferred to select a prism 318 with a high RI. For example, the prism 318 can be made of SF10 optical glass or sapphire when the range of wavelengths includes the visible spectrum. The prism 318 can be made of silicon or germanium when RI measurements are made using infrared wavelength sources. However, other materials can also be used. In addition, choosing a prism 318 with a high RI can improve wavelength resolution for long wavelengths where dispersion effects of the prism compromise TIR resolvability.

Although the prism 318 is illustrated as an equilateral prism, other types of prisms can be used. For example, a right angle prism such as a 30-60-90 prism can be used. It may be desirable to select a prism shape so as to avoid TIR of light at the prism-air interface at other prism surfaces. In some examples, the prism is a glass block or slab or a dielectric substrate that does not have a triangular-shaped geometry.

Referring to FIG. 3A, the optical beam produced by the cylindrical lens 312 is refracted, as shown by ray line 324, upon entering the prism 318. Light reflected off of the prism-sample interface 319 is directed along the axis 326 to a collimating lens system 385. The collimating lens system produces an optical beam that is collimated at least in the yz-plane as shown by ray lines 381, 383.

The collimated optical beam produced by the collimating lens system 385 is directed to an aperture plate 304 that defines a slit 305, which produces an optical beam associated with outermost ray lines 311, 313 in the xz-plane. FIG. 3B is a front enlarged view of the aperture plate 304 and illustrates the dimensions of the slit 305. As shown in FIG. 3B, the slit 305 has a shorter dimension 303 (width W) and a longer dimension 307 (length L) perpendicular to the shorter dimension in a plane defined by the aperture plate 304. The aperture plate 304 is situated within the refractometer 300 so that the longer dimension 307 is parallel to the x-axis.

In general, the dimensions of the slit 305 are selected in association with the angular spread of the optical beam from the collimating lens to minimize or reduce spectral overlap. Typically, the optical beam is substantially collimated and the slit width W is selected so as to reduce or eliminate spectral overlap in the diffracted optical beam produced by the diffraction grating 308. For example, the slit 305 can reduce the angular spread of the optical beam in the yz-plane to improve collimation. Wide slits are associated with greater spectral overlap and reduced spectral resolution, but do permit higher power in the diffracted optical beam.

Because the slit 305 can reduce the intensity of the optical beam received from the refractometer thereby reducing signal-to-noise ratio, it is generally preferred to select a relatively large slit width W. For example, the slit width W can be 10, 100, 200, 500 or 1000 times a central wavelength or other wavelength associated with the optical beam 381, 383. The slit length L is typically much larger than the width W and is selected based on the preferred size of the optical beam in the xz-plane. For example, the length L can be approximately the same size or greater than the aperture of the cylindrical lens 310 in the xz-plane. In some implementations, the slit 305 may not be needed. For example, spectral resolution of the refractometer 300 may be sufficient without use of the slit 305.

Referring further to FIG. 3A, the optical beam is received from the slit 305 by a diffraction grating 308. The grating 308 is situated so as to produce a spectrally dispersed beam that remains collimated within the xz-plane, as illustrated by ray lines 314, 315. Referring to FIG. 4, a groove layer 308A of the grating 308 includes grooves oriented parallel to the x-axis and parallel to the longer dimension 307 of the slit 305. The grating 308 diffracts the optical beam within the yz-plane, as illustrated by ray lines 330, 332, 334. The optical beam is spectrally spread by the grating 308 so that the wavelength of the spectrally dispersed optical beam varies in the yz-plane as a function of distance from (or angle of propagation relative to) an optical axis 306.

Although the grating 308 is illustrated as a transmissive grating, the refractometer 300 can be modified to instead include a reflective grating 308. In general, angular resolution of the refractometer depends at least in part on the dispersive effect of the grating 308. Thus, the grating 308 is preferably configured to produce a large dispersion. Since angular separation increases as groove or slit separation decreases, the grating can have a groove or slit spacing that is on the order of the wavelength being measured. For example, the spacing can be between about 1.5, 2, 3, 4 or 5 times the central wavelength or other wavelength associated with the optical beam 302.

The grating 308 can be an enhanced resolution transmission grating, a blazed grating, a holographic grating, or other spectrally dispersive element. Additionally, any other dispersive optical component configured to separate spectral components of an optical beam such as prisms can be used.

As shown in FIG. 4, the optical beam 302 can be oriented at an angle 301 relative to the optical axis 306. The angle 301 can be selected so that the range of wavelengths at which critical angle is being measured is approximately centered on the optical axis 306. For example, ray lines 330 and 334 represent the directions of propagation associated with maximum and minimum wavelengths within the selected wavelength range. Ray line 332 represents a direction of propagation of a central wavelength within the selected wavelengths range. Ray lines 330, 332, 334 are typically associated with a first diffraction order produced by the grating 308, but other diffraction orders can be used.

The spectrally dispersed beam produced by the diffraction grating 308 is received by a cylindrical lens 310 to produce a collimated, spectrally dispersed beam as indicated by ray lines 316, 317. The cylindrical lens 310 is positioned and oriented so as to collimate the spectrally dispersed beam in the direction of the diffraction produced by the grating 308. That is, the cylindrical lens 310 collimates the spectrally spread beam in the yz-plane, and the optical beam produced by the cylindrical lens 310 is also spectrally separated. For example, as shown in FIG. 4, the cylindrical lens 310 redirects the light propagating according to ray line 330 along ray line 340, the light propagating according to ray line 332 along ray line 342, and the light propagating according to ray line 334 along ray line 344. As shown, ray lines 340, 342, 344 are substantially parallel to but spatially separated from each other at the output of the cylindrical lens 310. As shown in FIG. 3A by the ray lines 316, 317, the optical beam produced by the cylindrical lens 310 is unchanged in the xz-plane and remains collimated in the xz-plane. Typically, the grating 308 and the cylindrical lens 310 are separated by a focal length of the cylindrical lens 310 so that the spectrally dispersed beam 314, 315 is collimated in the yz-plane.

The aperture of the cylindrical lens 310 can be selected so as to sufficiently collect diffracted light associated with the selected wavelength range. For example, the size and focal length of the cylindrical lens 310 can be selected so that, based on the divergence angles of the light 330, 334 and the separation between the grating 308 and the cylindrical lens 310, the range of wavelengths being measured is collected by the cylindrical lens 310 and has sufficient spatial separation. For example, it may be desirable to have the spatial separation of the wavelengths match the size of a detector 320, e.g. so as to fill the active area of the detector 320. In some implementations, the dispersive effect of the grating 308 can be increased by increasing the focal length of the cylindrical lens 310. In this manner, the spatial separation of the wavelengths is increased, independent of the angular spread of the wavelengths.

The optical beam produced by the cylindrical lens 310 is directed to a detector 320, such as a CCD sensor or other sensor capable of detecting the selected range of wavelengths. The detector 320 can be a full-field sensor, capable of generating a two-dimensional image from the detected light intensity.

In general, the resolution of the refractometer 300 can be increased by increasing the dimensions of the collimated, spectrally dispersed optical beam received by the detector 320 (i.e., the optical beam represented by ray lines 316, 317 in the xz-plane and by ray lines 340, 342, 344 in the yz-plane). The active area of the detector 320 can also be increased

13

correspondingly. The dimensions of the collimated, spectrally dispersed optical beam received by detector 320 depends on several factors, including the size and the focal length of the cylindrical lens 310 as well as the distance between the collimator 385 and the prism 318. For example, increasing the distance between the collimator 385 and the prism (i.e., the distance between the detector 320 and the prism 318 along the axis 326) can increase the dimensions of the collimated, spectrally dispersed optical beam 316, 317. In addition, increasing the focal length and size of the cylindrical lens 310 can increase the size of the collimated, spectrally dispersed optical beam. The refractometer 300 can be configured so that the size of the collimated, spectrally dispersed optical beam is such that the active area of the detector 320 is completely filled. In some implementations, the detector 320 may be configured to detect less than the entire range of angles of incidence. Although the detector 320 is illustrated as receiving light reflected at the interface 319 of the prism 318 and the sample 323, the refractometer 300 can be re-configured so that the detector 320 receives transmitted light. For example, the detector 320 can be positioned along the side of the prism 318 with the sample 323 and positioned in the path of refracted, transmitted light along the axis 326'.

Refractometers such as those illustrated in FIGS. 1-4 can also include polarizers and filters. For example, the refractometers can be configured so that the prism-sample interface is illuminated with polarized light and the light received by the detector is polarization filtered, where the polarization of the collected light is the same as that of the illumination light. Such a configuration may be useful for reducing detection of light scattered off the sample and/or prism-sample interface and can improve the resolution of the RI measurement. For example, by selecting a p-polarization for an optical beam, contrast between reflected and totally internally reflected angles can be enhanced.

Refractometers such as those illustrated in FIGS. 1-4 can be used for hyperspectral and/or real-time measurement of RI dispersion (i.e., the wavelength dependency of the RI). For example, the RI dispersion of a sample can be determined from a single refractometer image. In some examples, more than one image can be collected and used to determine RI. For example, signal to noise ratio can be improved by averaging images or by time-integrating each image. This can be referred to as instantaneous or nearly instantaneous RI measurement. Images can be collected in real-time or time integrated over a short time frame to generate real-time (or nearly real-time) video. In this manner, changes in RI dispersion can be detected as a function of time. This can be useful for the observation of chemical reactions or other time-dependent processes. Multi-wavelength RI measurement is enabled when the RI for more than one wavelength is calculated from an image. This can also be referred to as simultaneous measurement of RI over a range or plurality of wavelengths.

The measured dispersion profile can be continuous or discrete over a range of wavelengths, depending on the light source of the refractometer. That is, the measurement can be hyperspectral based on the light source and the range of wavelengths the refractometer is configured to detect. In addition, the RI measurement can be made over a range of wavelengths without scanning, rotating or other mechanized motion of optical components (e.g., neither the prism nor the sample needs to be rotated.)

The refractometers described herein can be configured to measure RI for ranges of wavelengths including but not limited to the visible spectrum. For example, the refractometers can be modified to measure RI over a range of infrared wave-

14

lengths. In this case, the optical components of the refractometer can be selected based on performance in the selected range of wavelengths.

Because RI is sensitive to temperature, the refractometers described herein can include temperature compensation. For example, a temperature correction factor can be calculated or otherwise determined for one or more of the optical components of the refractometer. Such a correction factor would represent the temperature sensitivity of the component over a range of temperatures. The correction factor could be incorporated into the RI calculations based on the temperature of the refractometer when the measurement was made. Alternatively, a refractometer can be situated in a temperature controlled environment.

The refractometers described herein, such as those illustrated in FIGS. 1-4, produce two-dimensional (2D) images with light intensity values that vary as a function of wavelength along a first axis and as a function of angle of incidence along a second axis. Therefore, wavelength and angle of incidence can be independently detected. For example, the first axis can be the y-axis and the second axis can be the x-axis. However, the first and the second axis need not be perpendicular. The pixels of the image can be mapped or calibrated to the range of wavelengths and range of angles of incidence detected. For example, each pixel y-value can be correlated with a wavelength value and each pixel x-value can be correlated with an angle of incidence value. Critical pixels can be determined for each wavelength value by identifying a position along the second axis (e.g., x-values) corresponding to the critical angle. Because refractive index can be determined from the critical angle using Snell's law, as discussed above, refractive index as a function of wavelength (e.g., dispersion) can be calculated using the identified critical pixels. By calculating the wavelength dependent RI for samples with known dispersion relationships, the refractometer can be calibrated for use with samples having unknown RI profiles.

FIG. 5 is a representative image 500 produced by a refractometer with no sample (i.e., air is the sample). The image 500 has been mapped to a representative range of wavelengths measured by the refractometer (400 nm to 700 nm) and to a representative range of RI measured by the refractometer (1.3 to 1.7). What follows is a discussion of an exemplary calibration procedure. The calibration procedure can be used to estimate RI from images generated by refractometers such as those illustrated in FIGS. 1-4.

In general, calibration involves two parts: (1) wavelength calibration (i.e., the correlation of pixel y-values to wavelength) and (2) refractive index calibration (i.e., the correlation of pixel x-values and y-values to refractive index).

Wavelength calibration can be accomplished using refractometer images generated with no sample (i.e., air is the sample) and one or more input light sources with known spectral intensities across the range of wavelengths at which RI is to be measured. For example, when calibrating a spectrometer to measure RI over the range of wavelengths from 400 nm to 700 nm, the wavelength calibration can be performed using two gas discharge lamps, such as Ne and Hg(Ar) lamps, as input light sources. One or more images are collected for each light source, and a composite image can be used for the wavelength calibration.

Each column of a collected image (i.e., the y-values for each x-value) corresponds to an emission spectrum for the input light sources. For example, a plot of pixel intensity versus pixel row number (i.e., y-value) corresponds to an emission spectrum. Each peak in such an emission spectrum can be associated with a wavelength value based on the known emission spectrum for the input light source(s),

15

thereby mapping pixel row number (i.e., y-value) to a range of wavelength values. Several columns can be selected and the row number (i.e., y-values) for each emission peak can be averaged. The averaged values can be used to derive a linear relationship (e.g., $\lambda(y)=a \cdot y+b$) between pixel row number (i.e., y-value) and wavelength (λ). (A relationship other than linear can be used, depending on the type of dispersion imposed by the grating or other dispersive component used in the refractometer.)

The wavelength resolution R_s of the refractometer can be represented as follows:

$$R_s = D \cdot R_p$$

where D is dispersion (nm/pixel) and R_p is pixel resolution. The dispersion D can be determined from the emission spectra or the derived $\lambda(y)$ relationship discussed above. Pixel resolution is determined by rotating the light source incidence angle on the grating (see, for example, angle **130** in FIG. **2**) so that zero-order diffracted light from the grating is detected by the CCD. The full-width at half maximum (FWHM) of this detected band of light is the pixel resolution R_p .

The wavelength resolution R_s depends on several factors, such as the detector and diffraction grating selected for use in the refractometer. For example, resolution can be improved by selecting a detector with low defects and high resolution, or large numbers of pixels and fine pixel spacing. CCD cooling and high bit data resolution may also improve wavelength resolution of the refractometer. In addition, resolution may be improved by increasing the dispersion of the grating. Wavelength calibration may not be necessary if the detector is capable of detecting wavelength with sufficient resolution.

Refractive index calibration can be performed using refractometer images generated from known samples by illuminating the prism-sample interface with an optical beam that includes the range of wavelengths over which RI is to be measured. Typically, several samples are measured with known refractive index values that extend through the range of values of interest. For example, for a refractometer to measure RI values between 1.3 and 1.7, samples having a range of RI values between 1.3 and 1.7 can be selected.

FIG. **6** illustrates three exemplary images for three different samples generated by a refractometer detecting reflected light off of the prism-sample interface. Light is incident on the prism-sample interface at a range of angles of incidence. This range of angles corresponds to the horizontal or x-axis of each image, such that each x-value corresponds to an angle of incidence. The images have been converted to binary to facilitate visualization of the critical angle. In the images, the white region (left side) corresponds to TIR and to angles of incidence greater than the critical angle. The dark region (right side) corresponds to the absence of TIR and to angles of incidence less than the critical angle. This light is mostly transmitted and only partially reflected by the interface between the sample and the prism. The boundary between the TIR region and the partial transmission region is indicated by numerals **610**, **620**, **630**.

The pixels that define the boundary between the light and dark region are referred to as critical pixels, and the x-values for the critical pixels correspond to the critical angles of the sample. As shown in FIG. **6** and by **610**, **620**, **630**, critical pixel location is a function of both x and y, demonstrating that critical angle (and therefore RI) varies as a function of wavelength. This dispersion relationship can be used to identify an unknown sample.

Critical pixel locations can be obtained by identifying the pixels corresponding to the transition between partial transmission and TIR that occurs at the critical angle of incidence

16

at the prism-sample interface. For example, techniques for extracting boundaries within an image can be used. Refractometer images can be averaged and converted to binary images, as shown in FIG. **6**. Critical pixel location can also be determined using a derivative and/or a Hilbert transform. Savitzky-Golay or other image filtering techniques can be used.

Using the extracted critical pixel locations and the known dispersion profile for each sample, refractive index can be expressed as a two-dimensional function of critical pixel location (x, y). For example, the measured dispersion profiles can be represented by Cauchy coefficients, and the derived refractive index function $n(x,y)$ can be quadratic in both x and y. The derived function $n(x,y)$ effectively maps the two dimensional refractometer image to RI for any given x and y-values, where x and y represent the location of detected critical pixels (i.e., critical pixel locations for a test sample image). Consequently, for test samples, RI as a function of wavelength is determined from critical pixel locations in the refractometer images.

FIG. **7** illustrates a representative method **700** of multi-wavelength measurement of refractive index of a sample. At **702**, a range of angles of incidence is selected. For example, the range of angles of incidence can be selected based on an expected range of critical angles for the sample. The range angles of incidence can be associated with a lens focal length. At **704**, a range of wavelengths is selected. At **706**, an optical beam that includes the selected range of wavelengths is directed to a prism-sample interface at the range of angles of incidence. For example, the directing of the optical beam can include focusing the optical beam at the interface thereby generating the range of angles of incidence at the interface. The range of angles of incidence can include a critical angle for the sample.

At **708**, an optical beam from the interface is spread so that the range of wavelengths and angles are independently detectable. For example, the optical beam can be light reflected from the interface. The spreading of the light can include spectrally dispersing or spreading the light along a first axis, and the directing of the light can include focusing of the light along a second axis. The first and the second axes can be perpendicular. At **710**, the spread light is imaged. For example, an imaging detector can receive the spread light and produce an image. At **712**, critical pixels are identified. For example, image pixels corresponding to a transition between TIR and partial transmission can be identified. At **714**, RI is estimated as a function of wavelength based on the identified critical pixels.

The method **700** need not be performed in the order illustrated in FIG. **7**. For example, the spreading of the light at **708** can be performed before the directing of the selected range of wavelengths at **706**. That is, at **706**, an optical beam including the selected range of wavelengths is spread. At **708**, the spread optical beam is directed to a prism-sample interface at the range of angles. For example, the spread optical beam can be focused on the interface. The spreading and directing of the optical beam are such that wavelengths and angles of incidence are independently detectable.

FIG. **8** illustrates a representative method **800** of refractometer calibration. At **802**, wavelength calibration image(s) are received. For example, wavelength calibration images can include one or more two-dimensional images collected using a refractometer with no sample and with one or more light sources having known emission spectra. At **804**, a wavelength-calibration relationship is determined. For example, the wavelength-calibration relationship can be an equation expressing wavelength as a function of one or more pixel

coordinates. The wavelength-calibration relationship can be based on the known emission spectra and the wavelength calibration images.

At **806**, refractive index (RI) calibration image(s) are received. For example, RI calibration images can include one or more two-dimensional images collected using the refractometer with one or more calibration samples having known refractive index dispersion profiles. At **808**, critical pixel locations are extracted from the RI calibration image(s). At **810**, refractive index as a function of critical pixel location, or $n(x,y)$, is determined. For example, $n(x,y)$ can be derived based on the known refractive index dispersion profiles of the one or more calibration samples.

Example Implementation

In a specific embodiment of the refractometer **100** of FIGS. **1A** and **2**, a quartz halogen fiber-optic light source produced a beam of collimated white light **102** that was received by the refractometer **100**. The optical beam **102** included a range of wavelengths from about 400 nm to about 700 nm. The slit **104** had a width W of 150 μm and was oriented with a long dimension **107** parallel to the grooves of a transmissive diffraction grating **108**. The diffraction grating **108** had a groove spacing of 830 grooves/mm. The optical beam **102** was incident on the grating **108** at an angle **101** of 27 degrees relative to the optical axis **106**. At this orientation, the grating **108** produced a diffraction pattern with 550 nm light directed along (and substantially parallel to) the optical axis **106**, along the ray line **132** and with 700 nm light and 400 nm light directed at approximately ± 7.15 degrees from the optical axis **106** along respective ray lines **130**, **134**.

The spectrally dispersed optical beam produced by the grating **108** was received by a 55 mm \times 25 mm cylindrical lens **110** with a focal length of 150 mm at a wavelength of 589.3 nm. The cylindrical lens **110** produced a collimated, spectrally dispersed optical beam that was spectrally spread in the yz -plane. That is, light having a wavelength of 400 nm (i.e., propagating along ray line **144**) and light having a wavelength of 700 nm (i.e., propagating along ray line **140**) were separated by about 37 mm. The distance between the cylindrical lens **110** and the grating **108** was approximately equal to the focal length of the cylindrical lens **110**. The collimated, spectrally dispersed optical beam was then received by a 25 mm \times 50 mm cylindrical lens **112** having focal length of 25 mm at a wavelength of 589.3 nm.

The cylindrical lens **112** focused the collimated, spectrally dispersed beam onto the prism-sample interface of a 60 mm equilateral dispersing prism **118** made of SF10 with a RI at 589 nm of 1.7667. The sample **123** was held in contact with the prism **118** using a sample holder **122**. The light reflected off the prism-sample interface was received by a non-cooled monochrome 39 megapixel full frame CCD. The captured images were digitized at 12-bit resolution by a timing board and transferred to a computer for processing using a frame grabber. The generated images included 5502 rows and 7344 columns of pixels.

Wavelength calibration was performed using Ne and Hg(Ar) gas discharge lamp as the input light sources and with air as the sample. The images were generated serially with the two sources. Eight different columns of the composite image were selected as emission spectra to be used for the calibration, and seven emission spectrum peaks were selected from each spectra. The wavelength values for each peak were averaged across the selected spectra, and the relationship between

pixel row number (i.e., y -value) and wavelength (λ) was calculated as follows:

$$\lambda(y)=-0.0554y+688.13.$$

The average standard deviation for the seven peaks was 7.5 pixels. The spectral emission lines were approximately 100 pixels wide (i.e., the full-width half max (FWHM) value) for Hg(Ar). The dispersion D was 0.056 nm/pixel, and the pixel resolution was determined to be 144 pixels. Thus, the refractometer resolution was calculated to be 6.38 nm.

Refractive index calibration was performed using 11 different samples with known RI dispersion profiles. The samples were characterized by the following RIs: $n=1.32, 1.35, 1.38, 1.41, 1.44, 1.48, 1.52, 1.56, 1.59, 1.62$, and 1.65. For each of these samples, the Cauchy coefficients were known. Images were acquired for each sample with a three second integration time. Critical pixels were extracted using the Hilbert transform and Savitzky-Golay filtering. Using the known Cauchy equation for each sample and the extracted critical pixel locations, the following empirical relationship was derived for refractive index:

$$n(x,y)=1.7474-3.5108\times10^{-5}x-7.0094\times10^{-7}y-4.2454\times10^{-9}x^2+1.7019\times10^{-9}y^2,$$

where x and y correspond to critical pixel location.

Subsequently, the RI of a validation or test sample was determined using three consecutive refractometer measurements and the RI relationship $n(x,y)$ shown above. The images were collected and critical pixel locations were extracted from the images using techniques described above for the known samples. The table below provides a comparison of the actual RI value for the validation sample, as determined from manufacturer-provided Cauchy coefficients, to experimental RI values.

$\lambda(\text{nm})$	Exp. RI	Cauchy RI	Difference	% Diff.
450	1.51260	1.51329	-0.00069	0.05
500	1.50647	1.50709	-0.00062	0.04
550	1.50102	1.50265	-0.00163	0.11
600	1.49762	1.49937	-0.00175	0.12
650	1.49610	1.49686	-0.00077	0.05

The maximum difference between the validation sample data and the actual RI computed from the Cauchy coefficients occurred at 414 nm and was 0.0036 units (0.24% of the actual RI). The variation between the three measurements was negligible (i.e., below the refractometer RI resolution), with an average standard deviation of 0.000132 and a maximum of 0.000743. The three second integration time used provided for an average image contrast ratio (CR) of 0.88 at about 90% max light source output, where $CR=(\text{max}-\text{min})/(\text{max}+\text{min})$ intensities. In comparison, CR was 0.01 for three milliseconds integration time.

The resolution of this refractometer system could be increased by using a zero-defect scientific-grade sensor, instead of an engineering-grade CCD sensor, and implementing CCD cooling. Additionally, the pixel data resolution of the evaluation electronics could be increased from 12-bits to 32-bits or higher. Furthermore, using a prism with a greater RI could improve resolution at longer wavelengths, where dispersion effects reduce the prism RI and therefore the TIR resolvability of the system. The use of a more intense light source could improve signal to noise ratio so that integration time could be reduced to durations more suitable for video frame rate (i.e., real-time or nearly real-time) RI measurement.

In view of the many possible embodiments to which the principles of the disclosed technology may be applied, it should be recognized that the illustrated embodiments are

only preferred examples and should not be taken as limiting the scope of the disclosure. We claim all that comes within the scope and spirit of the appended claims.

We claim:

1. A refractometer for multi-wavelength measurement of refractive index of a sample, comprising:

a dispersive optical system comprising a diffraction grating configured to spectrally spread an optical beam that includes a range of wavelengths by imposing a wavelength dependent angular dispersion along a first axis and a first cylindrical lens configured to collimate the spectrally spread optical beam along the first axis to produce a collimated spectrally spread optical beam; and

a focusing optical system configured to direct the collimated spectrally spread optical beam to be incident on an interface between the sample and a prism at a range of angles of incidence including a critical angle and further configured to focus the collimated spectrally spread optical beam along a second axis substantially perpendicular to the first axis so as to establish the range of angles of incidence and to produce a linear illumination pattern at the interface, wherein the linear illumination pattern is substantially parallel to the first axis and the wavelength of light of the linear illumination pattern varies as a function of distance along the first axis.

2. The refractometer of claim 1, further comprising:

a detector configured to receive the optical beam from the interface and to generate one or more two-dimensional images having pixel coordinates associated with the range of wavelengths and the range of angles of incidence.

3. The refractometer of claim 1, wherein the prism is an equilateral sapphire or SF10 prism.

4. The refractometer of claim 1, further comprising:

a light source configured to produce the optical beam and configured so that the optical beam is substantially collimated; and

a slit having a long dimension oriented substantially perpendicular to the first axis and configured to reduce spectral overlap in the spectrally spread optical beam.

5. The refractometer of claim 1, wherein the focusing optical system comprises:

a second cylindrical lens configured to focus the collimated spectrally spread optical beam along the second axis substantially perpendicular to the first axis so as to establish the range of angles of incidence and to direct the optical beam to the interface between the sample and the prism thereby producing the linear illumination pattern at the interface.

6. The refractometer of claim 1, wherein the linear illumination pattern at the interface is a focal line.

7. The refractometer of claim 1, wherein the diffraction grating is positioned to have grooves oriented parallel to the second axis.

8. The refractometer of claim 1, wherein the focusing optical system and the prism are configured to produce critical angle total internal reflection at the interface over at least a portion of the range of wavelengths.

9. The refractometer of claim 1, further comprising:

a sample holder configured to maintain contact between a surface of the prism and the sample and including a channel to enable flow-through of the sample.

10. A refractometer for multi-wavelength measurement of refractive index of a sample, comprising:

a dispersive optical system configured to receive a collimated optical beam that includes a range of wavelengths

and to spectrally spread the range of wavelengths of the received collimated optical beam along a first axis to produce a spectrally spread optical beam; and

a focusing optical system comprising:

a first cylindrical lens configured to collimate the spectrally spread optical beam along the first axis;

a second cylindrical lens configured to converge the collimated spectrally spread optical beam along a second axis that is not parallel to the first axis, to direct the collimated spectrally spread optical beam to be incident on an interface between the sample and a prism at a range of angles of incidence including a critical angle, and to produce a linear illumination pattern at the interface, wherein the wavelength of light of the linear illumination pattern varies as a function of distance along the first axis and wherein the prism has a surface configured to contact the sample at the interface and to receive the converged optical beam; and

a detection system situated and configured to detect critical angles of the sample for at least two wavelengths of the range of wavelengths based on portions of the converged optical beam received at the interface.

11. The refractometer of claim 10, wherein the second cylindrical lens and the prism are configured to produce critical angle total internal reflection at the interface over at least a portion of the range of wavelengths.

12. The refractometer of claim 10, wherein the prism is an equilateral prism.

13. The refractometer of claim 10, wherein the dispersive optical system comprises a diffraction grating having grooves oriented parallel to the second axis.

14. The refractometer of claim 13, further comprising:

a slit with a longer dimension oriented parallel to the second axis and configured to reduce spectral overlap of the spectrally spread optical beam produced by the dispersive optical system, wherein the slit is situated at an angle relative to the diffraction grating so that a first order of diffracted light is collected by the first cylindrical lens.

15. The refractometer of claim 10, further comprising:

a sample holder configured to maintain the contact between the surface of the prism and the sample and including a channel to enable flow-through of the sample.

16. The refractometer of claim 10, wherein the sample is a gas, a liquid or a liquid-gel.

17. The refractometer of claim 10, further comprising:

a light source configured to produce the collimated optical beam.

18. The refractometer of claim 10, wherein the prism is an equilateral sapphire or SF10 prism.

19. The refractometer of claim 10, wherein the detection systems is configured to generate one or more two-dimensional images having pixel coordinates associated with the range of wavelengths and the range of angles of incidence.

20. A method of measuring refractive index of a sample at a plurality of wavelengths, comprising:

receiving an optical beam that includes a plurality of wavelengths;

imposing a wavelength dependent angular dispersion on the optical beam along a first axis;

collimating the angularly dispersed optical beam along the first axis to produce a collimated spectrally dispersed optical beam; and

focusing and directing the collimated spectrally dispersed optical beam so as to generate a linear illumination pat-

21

tern substantially parallel to the first axis on an interface between the sample and a prism at a plurality of angles of incidence including a critical angle for one or more of the plurality of wavelengths, wherein the plurality of angles of incidence are established and the linear illumination pattern at the interface is generated by focusing the collimated, spectrally dispersed optical beam along a second axis that is not parallel to the first axis, wherein the wavelength of light of the linear illumination pattern varies as a function of distance along the first axis.

21. The method of claim 20, further comprising: identifying a critical angle for at least one of the plurality of wavelengths.
22. The method of claim 20, further comprising: determining a refractive index of the sample at at least one of the plurality of wavelengths.
23. The method of claim 20, further comprising: generating at least one two-dimensional image having a first axis corresponding to at least a portion of the plurality of wavelengths and a second axis corresponding to at least a portion of the plurality of angles of incidence.
24. The method of claim 23, further comprising: determining refractive index of the sample as a function of wavelength from the at least one two-dimensional image.
25. The method of claim 20, wherein the first axis is perpendicular to the second axis.

22

26. The method of claim 20, further comprising: receiving the optical beam from the interface between the sample and the prism; generating one or more test images associated with the received optical beam; identifying critical pixel locations from the one or more test images; and estimating refractive index for the test sample at at least two wavelengths of the plurality of wavelengths based on the identified critical pixel locations.
27. The method of claim 26, further comprising: deriving a wavelength-calibration relationship expressing wavelength as a function of one or more pixel coordinates based on wavelength calibration images collected with one or more light sources having known emission spectra, wherein the estimating of the refractive index is based on the wavelength-calibration relationship.
28. The method of claim 26, further comprising: deriving the refractive-index-calibration relationship based on a set of refractive index calibration images collected with one or more calibration samples having known refractive index dispersion profiles, wherein the refractive-index-calibration relationship expresses measured refractive index as a function of critical pixel location.

* * * * *